

short-wavelength light, such as blue or near-ultraviolet at wavelengths of 365, 405, or 436 nanometers.

[0176] As shown in the cross-sectional view of FIG. 14C, after development of the photoresist 226, the exposed area 224 of the photoresist is removed to the underlying silicon substrate 228. The remaining photoresist 226 is used as a mask during the selective removal of silicon dioxide 228. The silicon dioxide 228 is then etched by a fluorine-based plasma with a high degree of anisotropy and selectivity to the protective photoresist 226 until the silicon substrate 230 is reached as shown in FIG. 14D. As shown in FIG. 14E, a DRIE silicon etch creates a cylindrical region in the silicon substrate 200 that defines a reservoir 232. The reservoir 232 is etched to the desired depth. The remaining photoresist 226 can then be removed.

[0177] Completion of the Ejection or Nozzle Surface Processing

[0178] FIGS. 15A-15J illustrate the processing steps for the ejection or nozzle side of the substrate in fabricating the electrospray device of the present invention. Referring to the plan view of FIG. 15A, a mask is used to pattern 204 to define the through-substrate channels of the device. FIG. 15B is the cross-sectional view taken along line 15B-15B of FIG. 15A. A film of positive-working photoresist 208' is deposited on the silicon dioxide layer 210 on the nozzle side of the substrate 200. Referring to FIG. 15C, an area of the photoresist 204 corresponding to the entrance to through-substrate channels which will be subsequently etched is selectively exposed through a mask (FIG. 15A) by an optical lithographic exposure tool passing short-wavelength light, such as blue or near-ultraviolet at wavelengths of 365, 405, or 436 nanometers.

[0179] As shown in the cross-sectional view of FIG. 15C, after development of the photoresist 208', the exposed area 204 of the photoresist is removed and open to the underlying silicon layer 218 while the unexposed areas remain protected by photoresist 208'. Referring to FIG. 15D, a plasma enhanced chemical vapor deposition ("PECVD") silicon dioxide layer 233 is deposited on the reservoir side of the substrate 200 to serve as an etch stop for the subsequent etch of the through-substrate channel 234 shown in FIG. 15E.

[0180] This technique has several advantages over other techniques, primarily due to the function of the etch stop deposited on the reservoir side of the substrate. This feature improves the production of a through-wafer channel having a consistent diameter throughout its length. An artifact of the etching process is the difficulty of maintaining consistent channel diameter when approaching an exposed surface of the substrate from within. Typically, the etching process forms a channel having a slightly smaller diameter at the end of the channel as it breaks through the opening. This is improved by the ability to slightly over-etch the channel when contacting the etch stop. Further, another advantage of etching the reservoir and depositing an etch stop prior to the channel etch is that micro-protrusions resulting from the side passivation of the channels remaining at the channel opening are avoided. The etch stop also functions to isolate the plasma region from the cooling gas when providing through holes and avoiding possible contamination from etching by products.

[0181] Referring to FIG. 15E, the exposed areas 218 of the silicon substrate are then etched by a DRIE plasma with

a high degree of anisotropy and selectivity to the protective photoresist 208' to define through-substrate channels 234 until the reservoir 232 is reached. As shown in the cross-sectional view of FIG. 15F, the remaining photoresist 208' and 226 is removed from the silicon substrate 200.

[0182] Referring to FIG. 15G, the substrate 200 is subjected to an elevated temperature in an oxidizing environment to grow a layer or film of silicon dioxide 236 on the ejection or nozzle side of the substrate 200 and a layer or film of silicon dioxide 238 on all other exposed surfaces of the silicon substrate 200. Each of the resulting silicon dioxide layers 236, 238 has a thickness of approximately up to 2  $\mu\text{m}$ . As shown in FIG. 15H, the silicon dioxide layer 236 is then etched by a fluorine-based plasma until the silicon substrate 220 is reached. The silicon dioxide 238 on the surface of the through-substrate channels 234 serves as an etch stop for the subsequent DRIE etch of the silicon 220 of the silicon substrate 200. This allows for formation of longer nozzles (i.e., a deeper DRIE etch) with wall thicknesses less than 2  $\mu\text{m}$  over prior disclosed fabrication methods without accidental etching of the very thin silicon material that defines the nozzle wall thickness. FIG. 15I shows the DRIE etch of silicon 220 to form the recessed annular region 240 and the nozzles 242. FIG. 15J shows the removal of silicon dioxide layers 210, 212, 233 and 238 from the silicon substrate 200. The silicon dioxide layer 233 etch stop can be removed from the substrate by a hydrofluoric acid process.

[0183] An advantage of the fabrication process described herein is that the process simplifies the alignment of the through-substrate channels and the recessed annular region. This allows the fabrication of smaller nozzles with greater ease without any complex alignment of masks. Dimensions of the through channel, such as the aspect ratio (i.e. depth to width), can be reliably and reproducibly limited and controlled.

[0184] Preparation of the Substrate for Electrical Isolation

[0185] Referring to FIG. 16A, the silicon wafer 200 is subjected to an elevated temperature in an oxidizing environment to grow a layer or film of silicon dioxide 244 on all silicon surfaces to a thickness of approximately up to 3  $\mu\text{m}$ . The silicon dioxide layer serves as an electrical insulating layer. Silicon nitride 246 is further deposited as shown in FIG. 16B using low pressure chemical vapor deposition (LPCVD) to provide a conformal coating of silicon nitride on all surfaces up to 2  $\mu\text{m}$  in thickness. LPCVD silicon nitride also provides further electrical insulation and a fluid barrier that prevents fluids and ions contained therein that are introduced to the electrospray device from causing an electrical connection between the fluid the silicon substrate 200. This allows for the independent application of a potential voltage to a fluid and the substrate with this electrospray device to generate the high electric field at the nozzle tip required for successful nanoelectrospray of fluids from microchip devices.

[0186] After fabrication of multiple electrospray devices on a single silicon substrate, the substrate can be diced or cut into individual devices. This exposes a portion of the silicon substrate 200 as shown in the cross-sectional view of FIG. 16C on which a layer of conductive metal 247 is deposited, which serves as the substrate electrode. A layer of conductive metal 248 is deposited on the silicon nitride layer of the reservoir side, which serves as the fluid electrode.